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Ceramics International 27 (2001) 689–694

CERAMICS
INTERNATIONAL

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Effect of mullite formation on properties of refractory castables

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Received 2 November 2000; received in revised form 12 December 2000; accepted 1 February 2001

Abstract

In order to study the effect of the mullite bond phase on the physico-mechanical and refractory properties of the refractory castables, four castable samples were prepared; castable 1 contained 15 wt.% calcium aluminate cement (80% alumina) and 85 wt.% well graded tabular alumina . The other three samples (2, 3, 4) contained 10, 5 and 2% cement and 5, 10 and 13% of an alimina/ silica mixture (in the ratio 2.33:1, the molecular ratio of mullite). Their composition was investigated after firing at different firing temperatures using X-ray diffractin analysis. The physico-mechanical and refractory properties of such castables were determined according to standard specifications. Castable 4 that contained only 2 wt.% cement with 13 wt.% alumina/silica mixture and 85 wt.% well graded tabular alumina aggregate exhibited outstanding physico-mechanical and refractory properties after firing at 1500°C due to the presence of mullite in the bond phase with very little CaO. This enables their use in various refractory applications such as in steel, aluminium, copper, glass, cement, chemical and ceramic production. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: Mullite formation; Properties; Refractory castables

1. Introduction

In the last three decades, there was a greet interest in improving the quality of refractory concrete through decreasing the cement content, i.e. 4–8% in low cement castables (LCC) or 1–3% in ultra low cement castables (ULCC) or $<1\%$ in zero cement castables (ZCC). Decreasing the CaO content in these castables eliminates the disadvantages of the conventional castables (10–30%) such as high porosity, lower strength and slow controlled curing and drying processes resulting from their higher content of water in addition to the major drawback represented in their loss of strength during the dehydration process at 500–1000°C [1–4] . Moreover, the presence of a high content of CaO in conventional castables decreases the refractory properties due to the formation of low melting compounds at high temperatures. These disadvantages have been eliminated in the new generation of high technology castables which enables their use in a wide variety of applications.

Modern refractory concretes (LCC and ULCC) are complex mixtures of calcium aluminate cement, ultra fine materials, aggregates and admixtures. These concretes develop very high performance at heat and after heating. So, they are used when thermal shock resistance or resistance against abrasion and corrosion by slags or melting metals is required. These castables imply a good control of placing, i.e. rheology and hardening kinetics which are influenced not only by intrinsic reactivity of the calcium aluminate cement but also by the interactions between fillers and calcium aluminate cement [5–7].

In previous investigations [8–14], lower amounts of cement in conjunction with fine grain sized material having high surface area and dispersing aids were used. Those materials were silica fume, $A1_2O_3$,Cr_2O_3,ZrO_2, TiO_2, SiC, clay minerals and carbon. It was concluded that the presence of micro silica in the bond phase promotes low temperature strength as well as hot strength at intermediate temperatures. The good refractory properties such as volume stability, well balanced physical and hot mechanical properties and low cost promoted their use in a wide variety of refractory applications including aluminum melting furnaces, cement kilns and steel tundishes [15] . However, the sensitivity of the fumed silica-low cement castables with regard to water requirement and unpredictably short working time have caused

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PII: S0272-8842(01)00021-9

mixed reactions regarding their total acceptance and full utilization. One problem seems to be the lower refractoriness resulting from the formation of low melting compounds e.g. anorthite (1553°C) and gehlenite (1593°C).

The most frequently used fillers are fume silica and reactive alumina, so that they tend to form mullite after firing. The formation of mullite is of vital importance as mullite as a bonding phase exhibits high refractoriness, low creep rate, low thermal expansion and thermal conductivity, good chemical and thermal stability and good toughness and strength [16–17].

This work aims to improve the quality of refractory castables through the formation of mullite as a bonding phase in the final product.

2. Materials and experimental procedure

2.1. Materials

The materials used in this work are calcium aluminate cement (80% alumina) as a hydraulic binder, graded tabular alumina (30 wt.%; 6–10 mesh, 35 wt.%; 10–28 mesh, 10 wt.%; 28–48 mesh, 25 wt.% <48 mesh) as a refractory aggregate in addition to fine alumina (< 40 μm) and micro silica as additives. The chemical compositions and surface area of these materials are given in Table 1.

2.2. Procedure

Four castable samples were prepared, the first (conventional) contains 15 wt.% calcium aluminate cement and 85 wt.% tabular alumina aggregate. The other three compositions contain 10, 5 and 2% cement and 5, 10 and 13 wt.% of a 2.33:1 alumina:silica mixture, the ratio satisfying the mullite (A_3S_2)[1] formation at high temperature (Table 2). The castables were cast with the appropriate amount of water according to the "good ball in a hand" test [18].

The castables were cured in air at ambient temperature for 24 h then dried at 110°C for at least 6 h before firing.

Table 1
Chemical analyses and surface area data of the starting materials

Oxide (wt.%)	HAC (Lafarge)	FA (ALCOA)	FS (ECFA)
SiO_2	0.40	–	94.29
Al_2O_3	79.00	99.6	1.20
Fe_2O_3	0.25	–	1.16
CaO	20.0	–	0.56
MgO	0.20	–	1.60
Na_2O	0.20	0.10	0.01
L.O.I	–	–	1.30
S.A (m^2/g)	0.35	0.48	12.60

Table 2
Composition of the castable samples

	Composition (wt.%)			
	Cement	Fine alumina	Silica fume	Tabular alumina (aggregate)
Castable 1	15	–	–	85
Castable 2	10	3.5	1.5	85
Castable 3	5	7.0	3	85
Castable 4	2	9.1	3.9	85

Specimens 50×50×50 mm were cast so that physico-mechanical properties, namely bulk density (BD, g/cm^3), apparent porosity (AP,%) and cold crushing strength (CCS, kg/cm^2) of green and fired castables were measured according to DIN standard specifications [19–21].

After testing CCS, the fractured samples were crushed, ground and sieved to pass-76 μm sieve for X-ray diffraction (XRD) analysis. A Philips PW 1710 diffractometer using Ni- filtered Cu K_α radiation operating at 30 mA and 40 kV was used.

Thermal shock resistance of the prepared castables was measured using the "Bethlehem cycling test method" that measures strength loss after cycling prism samples from 1200°C to room temperature five times [22].

Creep deformation of the castable samples was determined according to DIN standard specifications [23].

3. Results and discussions

3.1. Composition of castables at different firing temperatures

Table 3 shows X-ray diffracion results (XRD) of the investigated castables at different firing temperatures (20, 1100,1400 and 1500°C) which show the following;

- In the green castable samples (20°C), the hydration products CAH_{10} and AH_3 could be characterized which decrease with the decrease in the cement content in a decreasing order; castable 1 > castable 2 > castable 3 > castable 4, in addition to α- $A1_2O_3$ and some CA_2. In castables 2,3 and 4, SiO_2 could be detected.
- After firing at 1100°C, the hydration products CAH_{10} and AH_3 are disappeared while the original phases CA_2 and α-$A1_2O_3$ are still present in addition to SiO_2 in castables 2, 3 and 4.
- At 1400°C, the formed anorthite phase (CAS_2) could be detected in castable 2 while mullite could be detected only in castables 3 and 4. In castable 1, recrystallization of the original phases CA_2 and α-$A1_2O_3$ is observed.

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[1] Cement notations are used; A: $A1_2O_3$, S: SiO_2, C: CaO, H: H_2O

Table 3
X-ray diffraction results of the castable samples at different firing temperatures[a]

	Temperature (°C)	CA_2	CAH_{10}	AH_3	α-Al_2O_3	SiO_2	CAS_2	A_3S
Castable 1	20	+ +	+ + +	+ + +	+	–	–	–
	1100	+ + +	–	–	+	–	–	–
	1400	+ + +	–	–	+	+q	–	–
	1500	+ + +	–	–	+	–	–	–
Castable 2	20	+ +	+ + +	+ + +	+ +	+	–	–
	1100	+ + +	–	–	+ + +	+	+	–
	1400	+ + +	–	–	+ + +	–	+ +	–
	1500	+ + +	–	–	+ + +	–	+ + +	–
Castable 3	20	+	+ +	+ +	+ + +	+ + +	–	–
	1100	+	–	–	+ + +	+ + +	–	–
	1400	+	–	–	+ + +	–	+	+
	1500	+	–	–	+ + +	–	+	+ +
Castable	20	+	+	–	+ + +	+ + +	–	–
	1100	+–	–	+ + +	+ + +	–	–	
	1400	+	–	–	+ + +	–	–	+ +
	1500	+	–	–	+ + +	–	–	+ + + +

[a] + + + Abundant; + + moderate; + little; –no.

- After firing at 1500°C, mullite (in castables 3 and 4), anorthite (in castable 2) and original recrystallized phases become more pronounced.

3.2. Physico-mechanical properties

3.2.1. Water of consistency

The water addition to a castable has a significant and direct influence on the final properties and castable specifications. Excess water can reduce strength and increase shrinkage, while too little water can produce voids in the castable, causes poor consolidation and placement which will produce a weak porous concrete [24]. Fig. 1 shows a significant decrease in the water/ solid (W/S) ratio as the cement content decreases i.e. from castable 1 to castable 4. The lower W/S ratio of castables containing incorporated fine alumina and silica fume (castables 2, 3 and 4) reflects improved particle packing effeciency in the castables. The particle packing increased as the amount of fine powders increased reaching its maximum and hence the minimum amount of the required mixing water in castable 4 which contained only 2 wt.% cement but 13 wt.% fine powders.

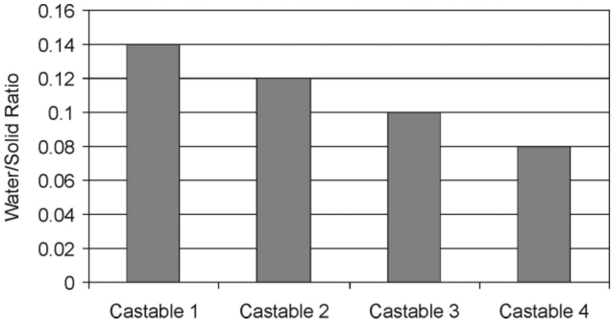

Fig. 1. Water/solid ratios of the investigated castable samples.

The thixotropic nature of low and ultralow-cement castables required that they have to be installed using either internal or external vibration. The flow properties during installation are critical as they have an important influence on physical properties such as density, porosity and strength. The castable will have good flow properties at low concentrations of mixing water and will form a homogeneous, well consolidated product [25].

3.2.2. Bulk density (BD) and apparent porosity (AP)

BD and AP values were determined for a range of firing temperatures (20, 400, 1100, 1400 and 1500°C). Fig. 2 shows that in castables containing the A/S mixture (castables 2, 3 and 4) there is an increase in the BD value accompainied by a decrease in the value of AP at each firing temperature. This behaviour becomes more obvious as the A/S content increases on the expense of the cement content. In the temperature range 20–1100°C, the previous behaviour is due to the finer particle size distribution of the A/S mixture that improves the packing effciency in the castable body. At a temperature $\geqslant$ 1400°C, the behaviour can be explained by the reactions that took place between alumina, silica and cement forming a liquid phase of the low melting point compound CAS_2 (1553°C) which fills the interspaces among the constituents of castable 2 and also the formation of mullite (A_3S_2) mineral with high density (3.16–3.22 g/cm^3) in castables 3 and 4, the combination of these two factors results in improved sintering after firing to high temperatures. Reduction in castable AP should lead to lower hot slag and metal penetration, reduced spalling, and, therefore, increased lining life in steel-making applications [26].

3.2.3. Cold crushing strength (CCS)

CCS results are presented as a function of firing temperature in Fig. 3 which shows the following:

- At 20°C, castable 1 containing 15 wt.% cement and no A/S mixture shows the highest values of CCS which is related to the higher amount of the cement hydrated products CAH_{10} and AH_3 that play the role of bonding. However, decreasing the cement content up to 5 wt.% does not affect much the CCS; in castable 3 containing 5 wt.% cement the CCS is reduced only by 9.2% compared with castable 1. This is due to the well packing achieved by the fine A/S powders in addition to the presence of considerable amounts of the hydrated products CAH_{10} and AH_3. Further decrease in the cement content to 2 wt.% (castable 4) results in a great detereoration in strength; it is reduced by 70.8% in comparison to castable 1, in this case the amount of cement is too small to obtain good bonding.
- At 1100°C; low CCS values of all castables is observed due to the breakdown of the hydraulic bond while no ceramic reactions could be started.
- At $\geqslant$1400°C; a completely different behaviour can be noticed. Castables 3 and 4 containing the least amounts of cements (5 and 2 wt.%, respectively)

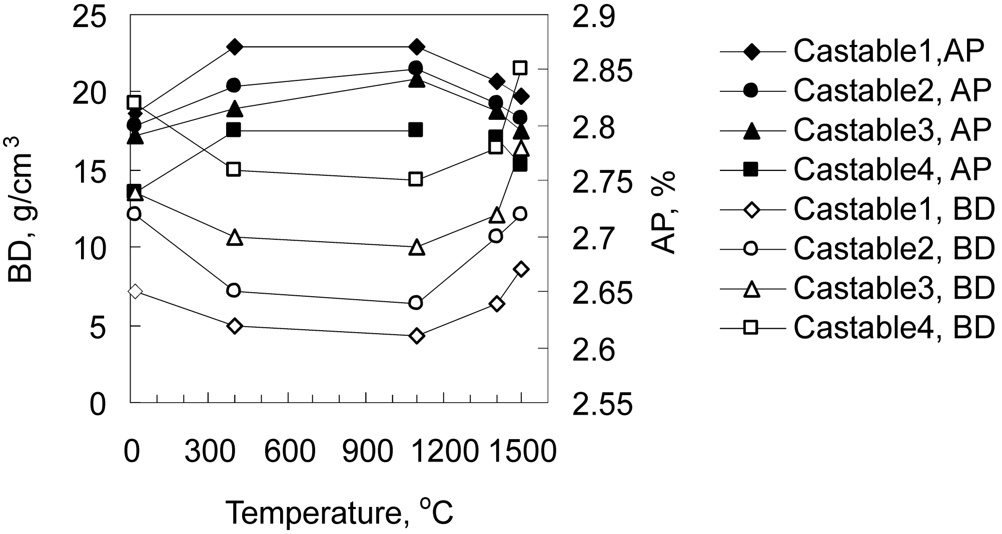

Fig. 2. Bulk density and apparent porosity of the castable samples fired at different firing temperatures.

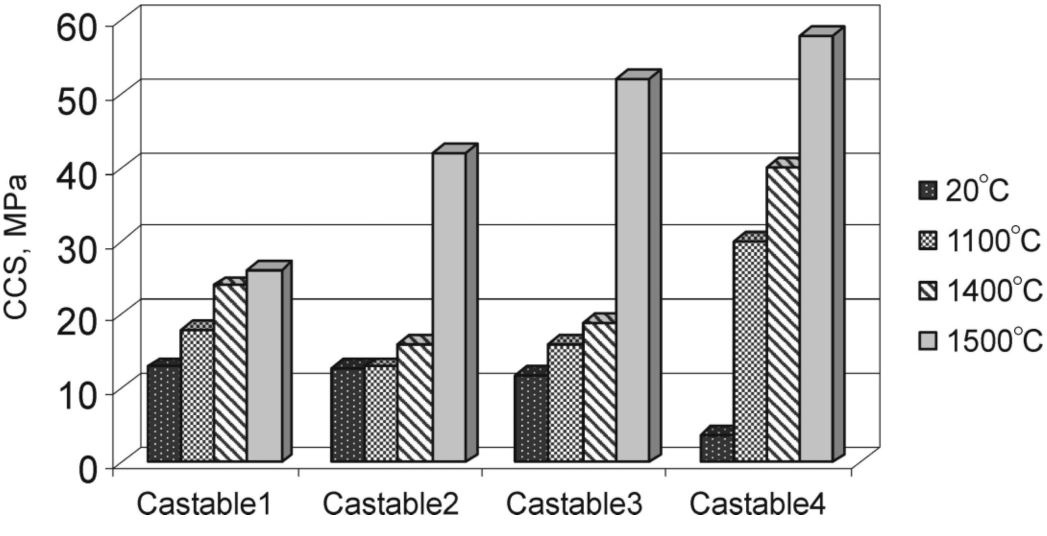

Fig. 3. CCS of different castable samples fired at different firing temperatures.

show the highest values of CCS which is certainly related to the formation of mullite mineral that forms a network of mullite needles which strengthens the structure at high temperature [27]. The higher CCS value of castable 4 compared with castable 3 is due to the presence of a relatively higher amount of mullite in the former. On the other hand, the presence of a higher amount of cement and hence calcia in castable 2 which attacks the mullite and inhibits its formation affects adversely the CCS. However, the formed CAS_2 liquid phase in castable 2 results in a slightly higher CCS than in castable 1 [28]. Another explanation is given by Schumacher [29] based on the volume increase of the alumina-silica when it is transformed to mullite. If the transformation takes place within a liquid phase, the expansion causes movement of the liquid. Therefore, more pores in the castables may become filled with liquid and may increase the volume fraction where mullite can develop and contribute to the bond. Such movement of the liquid phase may also be beneficial to the solution/precipitation process from which mullite is believed to develop.

Table 4
Thermal shock resistance "Bethlehem cycling test"

Castable no.	Strength loss (%)		
	Prefired to 1100°C	Prefired to 1400°C	Prefired to 1500°C
1	60	31	20
2	71	59	48
3	54	14	6
4	41	9	4

3.3. *Refractory properties*

3.3.1. *Thermal shock resistance*

For castables, the thermal shock resistance properties indicate prefiring conditions since strength loss behaviour can be highly dependent on the prefiring temperature. Table 4 shows the strength loss of of the investigated castables after three prefiring temperatures (1100, 1400 and 1500°C). The excellent thermal shock resistance noted for castables 3 and 4 after prefiring at 1500°C (loss in strength are only 6 and 4%, respectively) is attributed to the good distribution of the mullite bond from the reaction of microsilica and alumina. The poor resistance to thermal shock after prefiring at 1100°C is due to the absence of mullite which is formed at high temperature and the presence of crystallized silica left unreacted at the lower prefiring temperature. The better thermal shock resistance of castable 1 compared with castable 2 is attributed to the absence of crystallized silica in the first [15].

3.3.2. *High temperature creep deformation*

Fig. 4 shows the 1500°C creep behaviour of the investigated samples. Castable 4 shows the optimum creep properties, nearly straight forward behaviour due to the presence of mullite which promotes some expansion and volume stability at high temperatures, in addion to the limited amount of cement and hence calcia rich glassy phases with a low melting point. The other castables are greatly influenced by the presence of cement and are highly deformed. The relatively better behaviour of castable 1 compared with castable 2 is related to the absence of silica additives and hence lower rich calcia glassy phase in the first. Castable 3 which has a higher cement content than castable 4 shows relatively higher

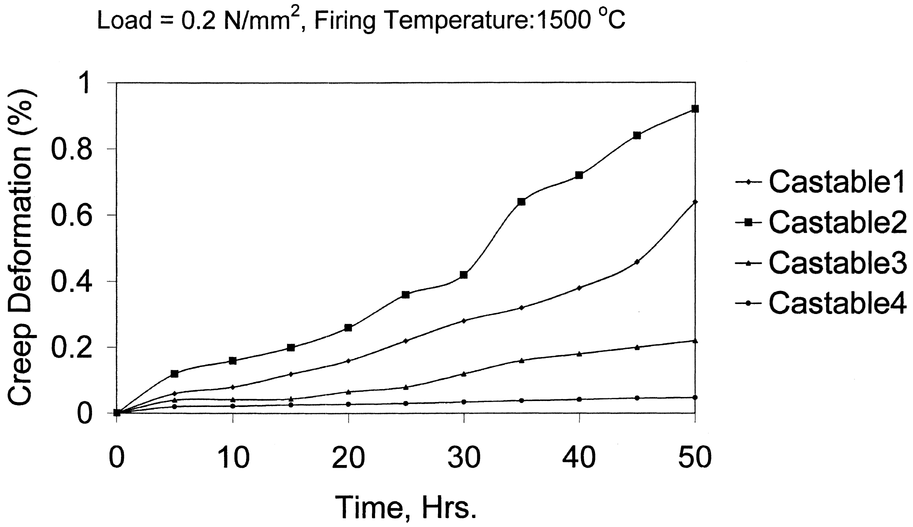

Fig. 4. Creep deformation of the fired castable samples.

deformation but better behaviour than castable 1 and 2 due to its content of the mullite bond phase.

4. Summary and conclusions

Physico-mechanical and refractory properties of castable samples containing A/S mixtures are very dependent on the content of cement and hence on the content of the A/S mixture in the castable. Castables containing 85 wt.% well graded tabular alumina as a refractory aggregate, 2 wt.% cement and 13 wt.% A/S mixture (2.33 alumina:1 silica) show improved physico-mechanical and refractory properties after firing at 1500°C. The presence of mullite in these castables is ubiquitous as the properties obtainable through ceramic processing and firing are outstanding. Mullite formed at high temperature as a bonding phase exhibits low creep rate, high thermal shock resistance and good sintering parameters with high CCS. These excellent properties of such castables enable their use in various refractory applications such as fabrication of steel, aluminium, copper, glass, cement, chemicals and ceramics.

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